Gadolinium-Loaded Plastic and Rubber Scintillators[1]

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ABSTRACT

This paper reports the fabrication of near UV-, blue-, blue-green-, and green-emitting polyvinyltoluene- and silicone rubber-based solid scintillators with sufficient gadolinium loading to make them attractive for the detection of thermal neutrons. Measurements of characteristic neutron-induced pulse height spectra (containing peaks corresponding to 29 keV conversion electrons coincident with gadolinium atomic x-rays), and the response of these scintillators to gamma rays will be described. In addition, the application of these new materials to measurements of radiation from plutonium and uranium will be discussed.

INTRODUCTION

Gadolinium has the highest thermal neutron absorption cross section of any naturally occurring element. It emits conversion electrons and atomic x-rays in over 50% of the neutron captures. The possibility of detecting these electrons and the accompanying atomic x-rays makes a detector based on gadolinium very attractive. Previous work[3,4,5] has focused on the use of gadolinium foils. However, these devices cannot distinguish between photoelectrons (Compton scattering and photoelectric absorption) and neutron-generated electrons because even the small thickness of foil introduces a considerable spread in the energy of the electrons as they exit the foil. Only an intimate mixture of the gadolinium and the detecting medium can guarantee the separability of neutron and photon events.

Organic liquid scintillators containing gadolinium are commercially available[6]. However, like all liquid scintillators, they must be handled with care, and stored and used in an oxygen-free and water-free environment. This means that containers for these liquids must be sealed, and that the liquids must be thoroughly bubbled with inert gas prior to sealing. In addition, these liquids sometimes contain organic solvents that require the storage container to contain no rubber or plastic parts. The liquids are also considered hazardous waste when they are to be discarded. Plastics on the other hand, typically are unaffected by moisture and air, require no encapsulation because they are solids, and generally are not considered hazardous waste because they are fully polymerized.

Surprisingly, a search of the literature turned up very few references to gadolinium-loaded solid organic scintillator. Czirr[7] reported a successful result using the benzoyl acetonate complex of gadolinium dissolved in a commercially available plastic scintillator. However, he also reports that the addition of the complex, even at the level of 0.2% by weight Gd, results in significant loss of light.

Aleshin, *et al.*,[8] report on the characteristics of large (5 - 8 cm diameter, 50 cm long) gadolinium-loaded polymethylmethacrylate (PMMA)-based scintillators. They do not report what compound

was used, but do indicate that the addition of gadolinium resulted in only slight degradation of light output. They also do not report the procedure for fabrication of their samples. For their experiments, gadolinium loading was between 0.8% and 2.1%.

Aleshin, *et al.*, also performed measurements of the sensitivity of their scintillator to unmoderated ^{252}Cf fission neutrons. Their large blocks of plastic scintillator acted as moderators to thermalize fast neutrons. In their experiments only neutron events that deposited at least 200 keV in the detector were accepted and so they were only sensitive to the simultaneous detection of multiple capture gamma rays. In this way they were more certain that the event was due to a capture.

Blank, *et al.*[9] (who were from the same Soviet institute that provided scintillator to Aleshin, *et al.* 10 years previously) describe a method for determining the concentration of gadolinium in PMMA-based scintillators. Their work seemed to be in support of a decades old (by the time of their writing) effort to use PMMA-based scintillators for fast neutron detection. Oddly, the only reference by Blank, *et al.* to scintillators for neutron detection *per se* is a reference to Czirr.

The goal of the present work has been to develop a method for the efficient and reliable production of gadolinium-containing scintillator disks. This has been accomplished in both plastic and silicone rubber. It was found that the same gadolinium compound was soluble in liquid scintillator and this too resulted in a useful product. In addition, it was found that by selecting a small size of detecting medium, conversion electrons (indicative of neutron capture) could be distinguished from the Compton continuum. The remainder of this report describes the fabrication procedure for plastic and rubber disks containing 1% by weight gadolinium, and the results of measurement of the neutron and photon response. The response of some of the liquids that were fabricated during the course of this work is also given.

PLASTICS AND LIQUID

Previous Soviet work indicated that PMMA was a useful carrier, and it is well known that it is transparent to light down to about 300 nm. However, loaded and unloaded material prepared with PMMA and 2,5-diphenyl oxazole (PPO) and other common scintillators were found not to be bright and yielded poor resolution. The behavior is attributable to the linear chain structure of PMMA and the polar nature of the molecule acting as a quencher for scintillations. It was necessary to use plastics with ring structures, such as polystyrene (PS) and polyvinyltoluene (PVT), that could couple energy to similarly structured organic fluors.

The general polymerization method for PVT began with the formation of a solution of Gd-containing compound and organic scintillator in the liquid monomer. Polymerization was effected by the addition of a peroxide initiator and the application of heat. To develop the optimum polymerization conditions for the preparation of optically clear, highly efficient, Gd-containing plastic scintillators, many factors, including temperature, reaction time, concentration and type of Gd-containing compound and scintillator, amount of initiator, and the use of an inert atmosphere or an aerobic environment were individually and independently addressed. As a rule, 1% - 1.5% primary scintillator, 0.5% - 1% initiator, anaerobic conditions, heating for 2 - 5 days at 50 - 60 ºC, and slow (~5 ºC/hr) cooling to room temperature were found to yield the best results with PVT disks. A photograph of two small disks is shown in Figure 1, below. The disks are clear, uncolored, and transparent.

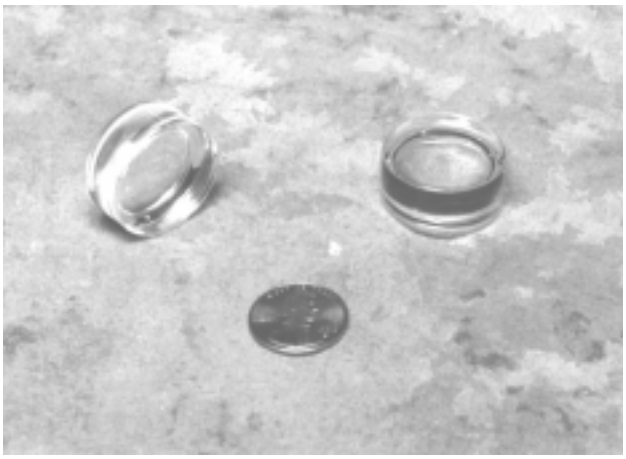

Figure 1, 2.5-cm diameter by 1-cm thick Gd-loaded plastic disks

The optimum ranges of Gd and scintillator concentration were determined experimentally using liquid solutions. This technique had the advantage that solutions were prepared rapidly. Solutions of pseudocumene (1,2,4-trimethylbenzene), PPO, and Gd-containing solute were prepared in 50-mm diameter cylindrical quartz cells having a 10-mm path length, mounted on a photomultiplier, and irradiated by gamma sources to establish a scale of energy deposition. Chart 1 shows the light output of 1% Gd-loaded scintillator as a function of PPO concentration. The different batches refer to three different preparations of gadolinium compound. It is seen that the brightness rises until about 1% PPO and then levels off (to within statistics), a consequence of self-absorption of the scintillation light. Similar measurements were performed with primary scintillators other than PPO, and to determine optimum concentrations of secondary and tertiary phosphors.

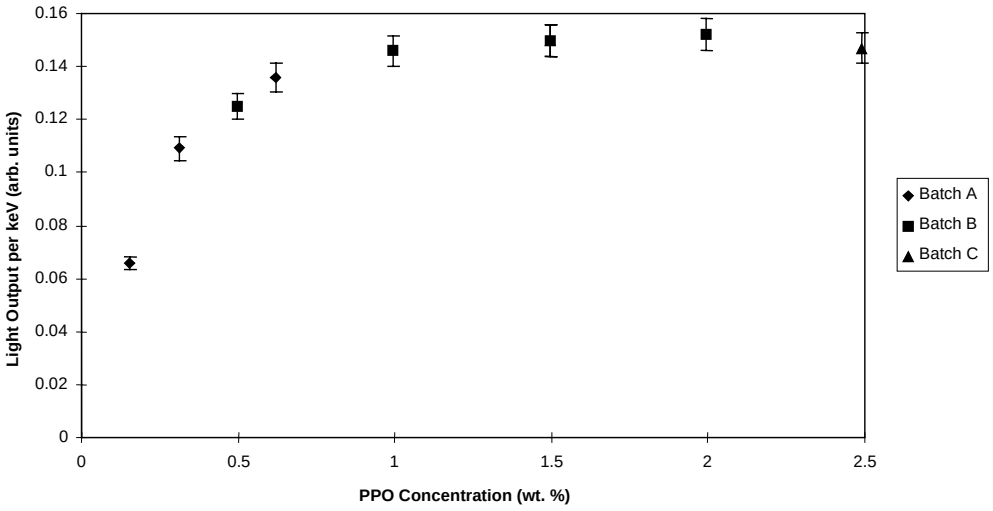

Chart 1, Variation of brightness with concentration of primary scintillator

RUBBER SCINTILLATOR

Silicone rubber based scintillators received considerable attention in the late 1980s and early 1990s in connection with their use in high-radiation environments. These rubbers polymerize at or slightly above room temperature, and have the advantages that they do not shrink on polymerization and, being flexible, are not prone to crazing. Therefore the problems of heat removal, and residual stress, inherent in the fabrication of plastics are not expected to be problems even when fabricating large pieces of rubber. In addition, Roff[10] indicates that silicones are stable to over 200 °C and so may have the added advantage that they may be usable in harsh environments. However, silicone rubber is not as strong a material as PS or PVT, and so may need to be encapsulated. Encapsulation would not be expected to be a difficulty since acrylic, polycarbonate, or even polystyrene plastics do not react with silicone fluids. Rubber polymerized in vessels made from such materials need not be removed from them and so the polymerization vessel and encapsulation could be one and the same.

Bowen, *et al.*[11], and Harmon, *et al.*[12], described the fabrication and testing of blue-emitting scintillators for high-energy physics experiments. These materials were estimated to be able to function even after exposures up to 10 megarads, far beyond the limit of exposure for PVT and PS. It was found that silicones were unaffected by radiation, while PS suffered 2% loss (relative to unirradiated material) at 450 nm and larger losses at shorter wavelengths. Bowen reports some scintillators emitting above 420 nm that were sufficiently soluble in silicone to be useful.

There are many varieties of silicone rubbers. However, to be useful as a scintillator carrier, it is necessary for the rubber to contain a moderate to high percentage of phenyl substitutions. Therefore, the highest phenyl concentration commercially available material (23% diphenylsiloxane, 77% dimethylsiloxane) was used. This silicone is a two-part fluid system with part A containing vinyl terminated poly(diphenyldimethyl)siloxane and part B containing methyl terminated poly(dimethylmethylhydro)siloxane. Polymerization is achieved at room temperature with the addition of about 1 :L divinyl platinum complex solution. The complex catalyzes the addition of the methylhydrosiloxane unit from part B to the terminal vinyl group on part A such that the silicon is added to one carbon of the vinyl group and the proton is added to the other carbon concurrent with a reduction of the carbon-carbon bond order from double to single. Thus, part A molecules form cross-links between different part B molecules. The unpolymerized fluid mixture is viscous and air entrained during mixing must be removed prior to solidification to avoid “freezing” bubbles in the disk.

Unadulterated part A and B fluids polymerize within seconds of the addition of catalyst. An unexpected observation was that the addition of PPO and gadolinium to the rubber increased the time to minutes to hours, depending on the concentrations of solutes. The typical procedure involved modest heating the fluids to facilitate dissolution of scintillator(s) and gadolinium compound followed by cooling to room temperature. Catalyst was then added and the mixture was placed in vacuum or centrifuge overnight. The resulting clear rubber was then heated for a short while to insure completion of polymerization.

Figure 2, Rubber scintillator samples in polymerization vials

Figure 2 shows examples of rubber scintillators. The leftmost sample actually is four individual disks polymerized sequentially one over the other; the optical interface between the topmost disk and the next is discernible. The leftmost sample contains blue-green and green secondary and tertiary scintillators; the other two are blue emitters. Experiments to determine the optimum concentrations of scintillators in the rubber were performed and results similar to those obtained with PVT were obtained. Typically, because of increased absorption of UV light, 1-cm thick silicone-PPO scintillators were about half the brightness of corresponding PVT samples.

GAMMA RAY AND NEUTRON RESPONSE

The gamma ray response of these scintillators is what would be expected for a low-Z material containing a small concentration of heavy metal. The responses of a 1% Gd-loaded PVT scintillator and a rubber scintillator to ^{241}Am are shown in Figures 3 and 4. The full energy peak is visible in both samples at 59 keV. However, although it is broader in the PVT because of the higher brightness, the resolution in the two samples are approximately equal. By 80 keV, photopeak efficiency is essentially zero.

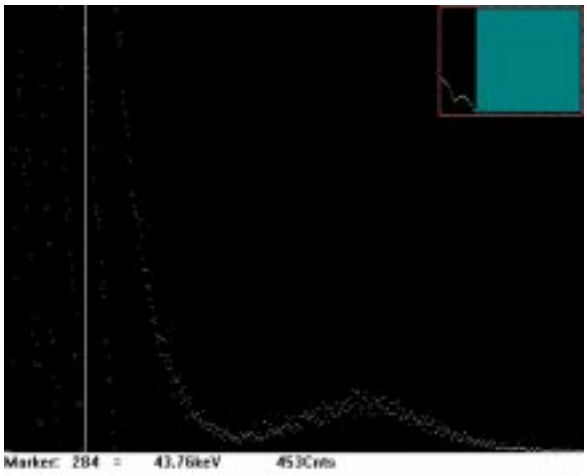

Figure 3, Response of PVT scintillator to ^{241}Am

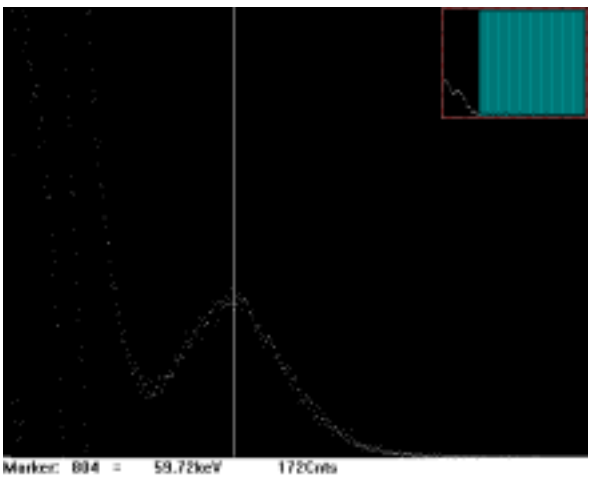

Figure 4, Response of silicone rubber scintillator to ^{241}Am

The neutron response of these scintillators is excellent. ^{155}Gd and ^{157}Gd are the two isotopes that are responsible for almost all of gadolinium's capture cross section. Both reaction products, ^{156}Gd and ^{158}Gd, are stable, and both have low lying (89 keV and 80 keV, respectively) first excited states through which the gamma ray cascade proceeds. Because of the high atomic number of gadolinium, there is appreciable probability of the production of conversion electrons when these first excited states decay, and the present work exploits these conversion electrons and the accompanying gadolinium atomic x-rays.

Consider the capture of a neutron by ^{157}Gd in a gadolinium-loaded scintillator. Following capture a shower of de-excitation gamma rays are emitted from the capturing nucleus. At the end of the cascade, either an 80 keV gamma ray or a 30 keV (80 keV minus 50 keV binding energy) conversion electron is emitted. Following the latter, the gadolinium atom de-excites by the emission of a 42 keV K x ray, and 8 keV in L, M, N, and lower energy x-rays. For all intents and purposes, all these events may be considered simultaneous.

The resulting spectrum of energy deposited in the scintillator depends strongly on where the capture event occurs in the scintillator. Since the mean free path of 42 keV photons in the scintillator is approximately 3 cm (at 1% Gd loading), there is a high probability that these K x-rays will escape the scintillator if the capture occurs near a surface. On the other hand, K x-rays generated by captures occurring near the center of the scintillator have a greater probability of absorption because of the longer distance to a surface. In addition, since the mean free paths of conversion electrons and lower energy x-rays are much less than 1 mm, these radiations are nearly always detected. Consequently, in a small scintillator the spectrum due to these processes consists of two peaks corresponding to 38 keV deposited (30 keV conversion electron plus 8 keV in low energy x-rays) and 80 keV (absorption of all energy). These features are immediately evident in Figure 5 (PVT) and Figure 6 (silicone), which shows the response to exposure to a thermalized Am-Li source.

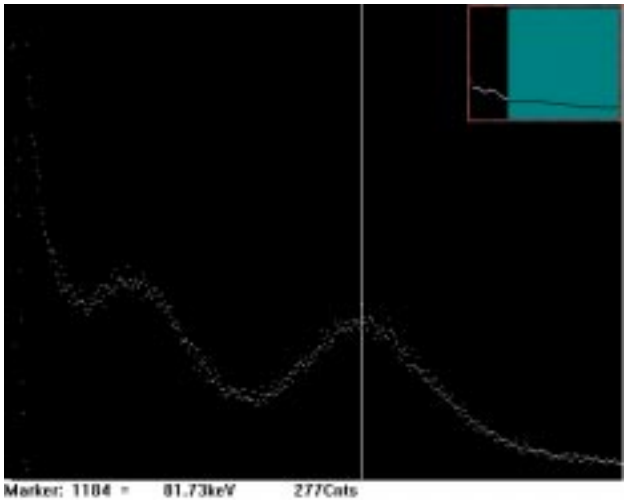

Figure 5, Response of PVT scintillator to neutrons

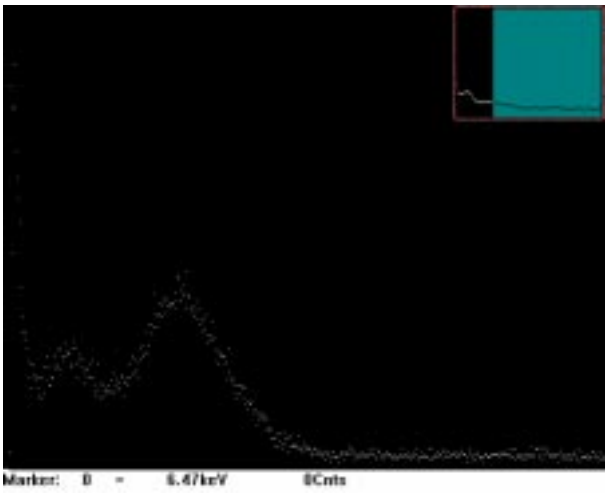

Figure 6, Response of silicone rubber scintillator to neutrons

The spectrum shown in Figure 5, however, contains a continuum in addition to the two peaks. This continuum arises from two sources. First, the radiation field in the source contains many gamma rays from neutron capture in a polyethylene moderator, cadmium outer shield, and tungsten source

shield. In addition, the tungsten shield emits gamma rays because of induced radioactivity. These gamma rays are energetic (most in excess of 400 keV) and, in general, generate only Compton events in the scintillator. The spectrum in a plastic scintillator from Compton events is essentially a continuum from zero energy up to the Compton edge (which depends on the incident photon's energy).

The second component of the continuum is because of the gadolinium itself, and its manifestation is more subtle. Because gadolinium is the source of a gamma ray cascade and is within the scintillator, all the cascade gammas have a chance of being detected. Some of the gamma rays are energetic and can contribute only a Compton continuum; some have only tens of keV of energy and may contribute conversion electrons; some have less than 10 keV and contribute their entire energy to the spectrum. However, the sum of energies (remember that since all these photons occur simultaneously as far as the detector is concerned their effect is seen as a sum of deposited energy) contributed by the cascade photons is a random variable because it is a stochastic process that determines which photon contributes how much energy. Consequently, each capture results in a random amount of energy deposited in the scintillators and a continuum spectrum occurs. Thus, to distinguish neutron events from photon events, it is necessary to make the detector volume sufficiently large so that all the 7.8 MeV from a neutron capture is deposited in the detector, or sufficiently small so that for the most part only conversion electrons and low energy x-rays are fully stopped in the detector. The spectrum shown in Figure 5 represents the latter case; the usual practice with large tanks of Gd-loaded liquid and the work of Aleshin, *et al.* represent the former. The spectrum in Figure 6 was obtained by subtracting the source-related continuum (measured by placing the scintillator in a Cd cup) from the spectrum. The response of liquid scintillators loaded with the same Gd compound exhibited the same features, but was brighter by about 50%. It was possible to load liquids to 4% Gd and still obtain a useful neutron response.

APPLICATION TO URANIUM AND PLUTONIUM

These scintillators offer an attractive alternative to ^{3}He tubes. The neutron response is readily discernible from the photon response by simple analysis of the pulse height spectrum. They are easily fabricated, relatively inexpensive (under $1.00/cc), black to thermal neutrons, and fast (they support high count rates). Containing large amounts of hydrogen and having a density of approximately 1 g/cc, they act as moderator and their incorporation in well counters would allow a reduction in the thickness and weight of the polyethylene used in present designs. They can be molded to near-net-shape and shape is limited only by light collection characteristics.

Silicone rubber scintillators offer the additional advantages of mechanical and chemical stability in the presence of a variety of solvents, flexibilty and stability over a wide temperature range, resistance to radiation damage, low shrinkage on polymerization, and polymerization at room temperature in the presence of oxygen. In addition, these scintillators can be trimmed with a sharp knife or scissors and they couple extremely well to silicone optical grease and directly to glass. The mechanical properties of silicone rubber make it possible build detectors that can be snaked into pipes and that can negotiate bends that might be beyond the abilities of rigid materials. The thermal and radiation resistance properties make this medium attactive for use in monitoring plutonium in storage.

An important additional advantage of silicones is that unadulterated silicone rubber can be used to make light pipes to couple photosensors to silicone rubber scintillators. Unlike PVT/lucite interfaces, the silicone scintillator/silicone light pipe optical interface is essentially lossless because of the match of indexes of refraction.

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